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Preprint

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*To be presented at the NCPV Program Review Meeting
Lakewood, Colorado
14-17 October 2001*



NREL

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1617 Cole Boulevard
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Contract No. DE-AC36-99-GO10337

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High-Efficiency CTO/ZTO/CdS/CdTe Polycrystalline Thin-Film Solar Cells

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ABSTRACT

Cadmium telluride is a promising photovoltaic material for thin-film solar cells. However, the performance and reproducibility of devices has been limited by the conventional $\text{SnO}_2/\text{CdS}/\text{CdTe}$ device structure used for more than 30 years. In this paper, we report that the device performance and reproducibility of CdTe cells can be improved by using a modified CTO/ZTO/CdS/CdTe device structure developed at NREL. We achieved high FF of 77.34% and high J_{sc} of near $26 \text{ mA}/\text{cm}^2$, and fabricated a CdS/CdTe polycrystalline thin-film solar cell demonstrating an NREL-confirmed, total-area efficiency of 16.5%. This is the highest efficiency ever reported for CdTe solar cells.

INTRODUCTION

Cadmium telluride has been recognized as a promising photovoltaic material for thin-film solar cells because of its near optimum bandgap of $\sim 1.5 \text{ eV}$ and its high absorption coefficient. Small-area CdTe cells with efficiencies of more than 15% [1] and commercial-scale modules with efficiencies of $>10\%$ [2] have been demonstrated. However, the performance and reproducibility of CdTe cells have been limited by the conventional $\text{SnO}_2/\text{CdS}/\text{CdTe}$ device structure that has been used for more than 30 years. For example, conventional transparent conductive oxides, primarily SnO_2 films, have an inherent sheet resistivity of $\sim 10 \text{ } \Omega/\text{Sq}$ and an average transmission of 80%. This does not provide adequate design latitude when trying to optimize either device performance or manufacturing cost. The CdS window layer has a lower bandgap ($\sim 2.4 \text{ eV}$) that causes absorption in the short-wavelength region. Higher short-circuit current densities (J_{sc}) can be achieved by reducing the CdS thickness to improve the blue response in the conventional CdS/CdTe device structure. However, reducing the CdS thickness can adversely impact device open-circuit voltage (V_{oc}) and fill factor (FF). Finally, it is well known that the CdCl_2 treatment is important for making high-efficiency CdTe devices. However, one disadvantage of the CdCl_2 -treatment is that over-treatment can result in loss of adhesion. The adhesion problems can limit the optimal CdCl_2 treatment process, as well as device performance.

In the last five years, we have tried to understand and solve these issues related to conventional $\text{SnO}_2/\text{CdS}/\text{CdTe}$ device structure. We developed several novel materials and a modified CdTe device structure. First, we developed a novel process to prepare high-quality cadmium stannate (Cd_2SnO_4 , or CTO) transparent conductive oxide (TCO) films, which have lower resistivity, higher transmittance and smoother surfaces than conventional SnO_2 TCO films [3-5]. When replacing the SnO_2 TCO film with a Cd_2SnO_4 film in

a CdTe cell, J_{sc} and FF of CdTe cells can both be improved [6-8]. Second, we developed and integrated the high-resistivity zinc stannate (Zn_2SnO_4 , or ZTO) buffer layer into CdTe cells, which improved device performance and reproducibility [9-11]. Third, we developed and integrated modified CdS films with higher optical bandgap into CdTe devices. This improved blue quantum efficiency and J_{sc} . Fourth, we developed a modified CTO/ZTO/CdS/CdTe device structure and made high-efficiency CdS/CdTe polycrystalline thin-film solar cells [12]. Finally, we developed a novel manufacturing process for fabricating high-efficiency CTO/ZTO/CdS/CdTe solar cells with potential for low cost and high throughput [13-14].

In this paper, we present the updated high-efficiency device results and give some examples to explain how the modified CTO/ZTO/CdS/CdTe device structure works for achieving the high performance and good reproducibility.

EXPERIMENTAL

Both CTO and ZTO films were deposited by rf magnetron sputtering at room temperature in pure oxygen using commercial hot-pressed oxide targets. The CTO film was treated at $580^\circ\text{--}660^\circ\text{C}$ for 10-20 minutes in CdS/Ar atmosphere. The thickness of both CTO and ZTO films was varied from 100 to 300 nm. The CdS and CdTe films were prepared by chemical bath deposition (CBD) and close-spaced sublimation (CSS) techniques, respectively. The CdTe film was deposited at $570^\circ\text{--}625^\circ\text{C}$ for 3-5 minutes in O_2/He mix atmosphere. After CdTe deposition, samples received a vapor CdCl_2 treatment at $400^\circ\text{--}430^\circ\text{C}$ for 15 minutes. $\text{CuTe}:\text{HgTe}$ -doped graphite paste, followed by a layer of Ag paste, was then applied to the devices as the back-contact layer.

UPDATED DEVICE RESULTS

1. High FF

Table 1 lists current-voltage parameters of two high-efficiency CdTe cells with FF of more than 77%. These are the highest FF values ever reported for CdS/CdTe polycrystalline thin-film solar cells. Device analyses from NREL and Colorado State University [15] indicate that these cells with high FF have lower series resistivity R_s ($\sim 1 \text{ } \Omega \text{ cm}^2$), higher shunt resistivity R_{sh} ($\sim 3\text{--}5 \times 10^3 \text{ } \Omega \text{ cm}^2$), and better diode quality factor A (~ 2).

It is well known that reducing TCO resistivity is essential for reducing R_s and improving FF in superstrate devices.

Table 1. NREL standard I-V measurements

Cell#	V_{oc} (mV)	J_{sc} (mA/cm^2)	FF (%)	η (%)	Area (cm^2)
W561-B	842.1	24.12	77.26	15.7	1.001
W562-B	848.1	23.97	77.34	15.7	0.976

We have reported previously that cadmium stannate TCO films have resistivities ($\rho \sim 1.5 \times 10^{-4} \Omega \text{ cm}$) that are two to six times lower than SnO_2 films [3-5]. It is thus obvious that by replacing the SnO_2 with a CTO TCO film, the R_s can be reduced. Also, low-resistivity CTO films will allow us to increase the width of the sub-cell in modules, thereby increasing total-area module efficiency.

Integrating a ZTO buffer layer can significantly improve R_{sh} in two ways [9-11]. First, it reduces the probability of forming a localized TCO/CdTe junction with low V_{oc} and FF when the CdS film is thinned. Second, the ZTO buffer layer can act as an “etch-stop” layer during the back-contact formation process and greatly reduce shunting problems.

2. High J_{sc}

Table 2 lists I-V parameters of two high-efficiency CdTe cells with high J_{sc} of near 26 mA/cm^2 .

Table 2. NREL standard I-V measurements

Cell#	V_{oc} (mV)	J_{sc} (mA/cm^2)	FF (%)	η (%)	Area (cm^2)
W547-A	847.5	25.86	74.45	16.4	1.131
W567-A	845.0	25.88	75.51	16.5	1.032

In this work, high J_{sc} 's have been achieved by three ways: reducing J_{sc} loss due to TCO absorption, reducing J_{sc} loss due to CdS absorption, and reducing J_{sc} loss due to recombination in the junction and CdTe regions.

(1) We have reported previously that Cd_2SnO_4 TCO film has higher transmittance and lower absorbance than SnO_2 films [6-8]. Table 3 lists the J_{sc} loss due to TCO absorption for four different TCO films that are all deposited on Corning 7059 glass. It can be seen that the CTO film has the lowest J_{sc} loss (0.6 mA/cm^2) – two to four times lower than SnO_2 films prepared by precursors TMT and SnCl_4 , respectively. Also, we can see that integrating a ZTO buffer layer into a CdTe cell results in a J_{sc} loss of $<0.1 \text{ mA/cm}^2$ due to its high bandgap and low absorption [9-11].

Table 3.

TCO	R_s (Ω/Sq)	J_{sc} loss due to TCO absorption
SnO_2 (SnCl_4)	8-10	2.8
SnO_2 (TMT)	7-8	1.3
Cd_2SnO_4	7-8	0.62
CTO/ZTO	7-8/ $\sim 10^5$ - 10^6	0.68

(2) In the conventional $\text{SnO}_2/\text{CdS}/\text{CdTe}$ device, improved blue spectra response can be achieved by reducing the CdS thickness. However, reducing CdS thickness can impact device V_{oc} and FF, and reproducibility. In the CTO/ZTO/CdS/CdTe device, interdiffusion between the CdS and ZTO films “consumes” CdS film during device-fabrication. This interdiffusion can occur either at higher temperature (570° - 650°C) in Ar, or at lower temperature (400° - 420°C) in a CdCl_2 atmosphere [10,12]. Therefore, we can control CdS consumption by optimizing CdTe deposition and CdCl_2 treatment process. Using this technique has resulted in internal quantum efficiencies of $>75\%$ at 400 nm and reduced J_{sc} loss due to CdS absorption to 1.0 - 1.3 mA/cm^2 . This property may also be exploited in production by using thicker CdS films, thereby enhancing yield without reducing J_{sc} .

(3) The interdiffusion between the CdS and ZTO layers also significantly improves the adhesion between the TCO and the CdS layer after CdCl_2 treatment [10-12]. This improvement not only improves the device reproducibility, but also provides greater latitude in optimizing the CdCl_2 treatment process. The time-resolved photoluminescence (TRPL) results indicate that an optimally CdCl_2 -treated device has much longer TRPL lifetime, and thus, lower junction recombination. Indeed, J_{sc} loss due to recombination in the junction regions is only $\sim 0.5 \text{ mA/cm}^2$.

3. High efficiency

A number of CTO/ZTO/CdS/CdTe cells with efficiency of more than 15.8% have been fabricated. We have demonstrated a CTO/ZTO/CdS/CdTe polycrystalline thin-film solar cell with an NREL-confirmed total-area efficiency of 16.5% ($V_{oc}=845.0 \text{ mV}$, $J_{sc}=25.88 \text{ mA/cm}^2$, $\text{FF}=75.51\%$, and $\text{area}=1.032 \text{ cm}^2$). We believe that this is the highest efficiency ever reported for CdTe solar cells.

CONCLUSIONS

The use of a modified CTO/ZTO/CdS/CdTe device structure can minimize some issues that are significant in conventional $\text{SnO}_2/\text{CdS}/\text{CdTe}$ cells and can improve device performance and reproducibility. A CTO/ZTO/CdS/CdTe cell with an NREL-confirmed total-area efficiency of 16.5% has been achieved, which is the highest efficiency ever reported for CdS/CdTe solar cells.

ACKNOWLEDGMENTS

The authors would like to thank Prof. Sites and C. Jenkins at CSU for device characterization. This work is supported by the U.S. Department of Energy under Contract No. DE-AC36-99GO10337 to NREL.

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